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ABSTRACT

In our development of a field deployable infrared isotope ratio spectrometer (IR2) for compound specific isotope analysis (CSIA), the IR2's accuracy and stability have reached a stage that small fractionation in reference gas pulses generated as standard are observed easily and repeatedly. Such fine fractionation is often difficult to observe in regular Isotope Ratio Mass Spectrometer (IRMS) due to instrument drift on the order of 10s of minutes. After careful design of reference pulse sequences and long period of data collection, such fractionations are also verified in a commercial continuous flow CSIA-IRMS. Implications of the fractionation and observation process are discussed.

KEY WORD LIST

green photonics, quantum cascade laser; laser spectroscopy, Hollow Waveguide; Compound Specific Isotope Analyzer

INTRODUCTION

Field deployable compound specific isotope analysis (FD-CSIA) has many applications in fossil energy exploration, food and drug identification, environmental protection and human health care. We have been developing such an instrument based on hollow waveguide (HWG) and mid-Infrared quantum cascade (QC) lasers, i.e. Infrared Isotope Ratio (IR2) spectrometer which is based on absorption spectroscopy and coupled with gas chromatograph (GC) to realize FD-CSIA instrument[1, 2]. Instruments for individual gas isotope analysis, e.g. CO_2 and H_2O, based on optical absorption spectroscopy have already been commercialized, and they have demonstrated better field operational capabilities. One of the advantages of such optical absorption based instrument is to be able to conduct measurement without frequent reference calibration[3], and this advantage lies in the fact that the Beer's law that this kind of instruments rely on which could effectively calibrate out drifts which otherwise will be hard to remove with mass spectrometry based instruments. For practical application, it is also desirable for conventional optical absorption based instrument to operate with minimal calibration because the sample cells usually are large, i.e. 10s or even 100s of ml and frequent calibration will take much longer time and consume lots of reference gases. The large sample cell volume also means such optical absorption based platform is not compatible with capillary based chromatographs, where the sample volume is often limited to μL or less. In principle, our IR2 spectrometer and resulting CSIA instrument should also require less frequent calibration, although the small sample cell volume, i.e. 100s of μl, enables fast calibration with minimal consumption of reference gases. Such small sample cell volume, a unique feature of HWG and QC laser based platform, could make Mid-Infrared optical absorption based spectrometer compatible with capillary chromatographs. This unique feature could improve the detection limit of GC-IR (Infrared) close to that of GC-MS (mass spectrometery), and at the same time requiring minimal internal standard or calibration.

In stable isotope analysis, pulses of reference gases are used for calibration all the time to ensure the integrity, stability of the measurement over long period of time. This is especially vital for Isotope Ratio Mass Spectrometer (IRMS), and in fact, the classic dual inlet offline IRMS has an accuracy almost an order of magnitude better than GC coupled online IRMS because the dual inlet IRMS does more frequency calibration than online IRMS which only calibrate at the end or the start of a GC run, i.e. every 10 minutes to an hour.

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Here, our IR2 has demonstrated the stability and accuracy that enable easy observation of some fine fractionations during reference gas pulses generation; whereas such fractionations are hard to observe with online IRMS due to the relatively large drift associated with mass spectrometry.

EXPERIMENT

Latest progresses in IR2 spectrometer reduce system weight and power consumption

Recently, noticeable progress has been made in QC lasers in the range of 2,300cm^{-1}. The devices could now working in continuous wave (CW) mode at above room temperature up to 70°C[4] and with power consumption less than 1W[5]. These results enable us to replace old CW QC lasers which need to be cooled down to -20°C, and the savings in Peltier cooling power translate into total saving in system temperature control power from 300W to only 15W! In fact, we are no longer cooling the spectrometer box and QC lasers, and only small heating power is needed to maintain the spectrometer temperature. With better insulation, we expect the total power to maintain temperature of the spectrometer, including powering and temperature control for the laser, will be reduced to less than 12W!.

With the HWG platform, we could pump down the IR2 spectrometer system with a pair of micro diaphragm pump, e.g. Hargraves CTS pump, while maintaining a sample refresh rate higher than 10Hz. These micro diaphragm pumps consume less than 5W average power and weigh less than 200grams.

Now, an IR2 spectrometer with total power consumption less than 20W and weighs less than 10 pounds is being designed. This opens the possibility to transport the IR system to many places previously impossible, e.g. airborne systems on UAVs.

Improved stability allows accurate measurement during a long GC run

In the past 3 years, we have developed the online continuous flow CO_2 Infrared Isotope Ratio (IR2) sensor module for GC using QC laser and HWG; we have succeeded in using a CW QC laser for simultaneously measuring ^{12}CO2 and ^{13}CO2 at ~2,299.70cm^{-1}. The instrument is now able to measure δ^{13}C with an error within ±0.2 per mil for a hydrocarbon compound coming out of a GC. One of the major challenges in coupling IR2 with GC is to ensure the stability of the IR2 spectrometer during a GC run lasting 10s of minutes, since reference gas calibration could not be practically carried out throughout the GC run, and only limited to the beginning or the end of the GC run. Here, we demonstrate the stability of the IR2 spectrometer is already comparable or at certain scenario better than IRMS, i.e. fine fractionation could be easily observed during reference gas pulse generation.

RESULTS

IR2 spectrometer easily observed fractionation in reference pulse generation

We programmed our GC-IR2 system with a GC run that has two reference pulses inserted before the samples coming out of the GC (see figure 1a). Accidental typo made the two reference pulses of different pulse widths, i.e. 60 seconds and 10seconds, and to our surprise, the values of the two pulses repeatedly differ by ~0.25‰ for several GC runs. The reference pulses are generated by an automated 3-way Swagelok ball valve with 1/8" tubing, which switch between GC elute mode and reference gas mode, and the reference pulse width is controlled by the GC-IR2 computer. The reference gases are 3% or 1% CO_2 buffered with pure air, and we could adjust the flow rate read on a Thorpe tube flow meter by changing the backing pressure and a needle valve.

We then proceed to verify this is indeed a real fractionation by testing GC run with reference pulses of different pulse widths only (figure 1b). In this GC run lasting 2,700 seconds, we group 4~8 reference pulses of same pulse width together, i.e. 7 pulse width values of 10 sec, 5 sec, 20 sec, 40 sec, 80 sec, 160 sec and back to 10 sec at the end of the GC run. The measured $^{13/12}$C values are grouped according reference pulse widths, and fractionation according to pulse width is obvious (figure 2a). At low pressure and slow flow, the fractionation could be as large as 1‰ when the pulse width varies from 5seconds to >100seconds.

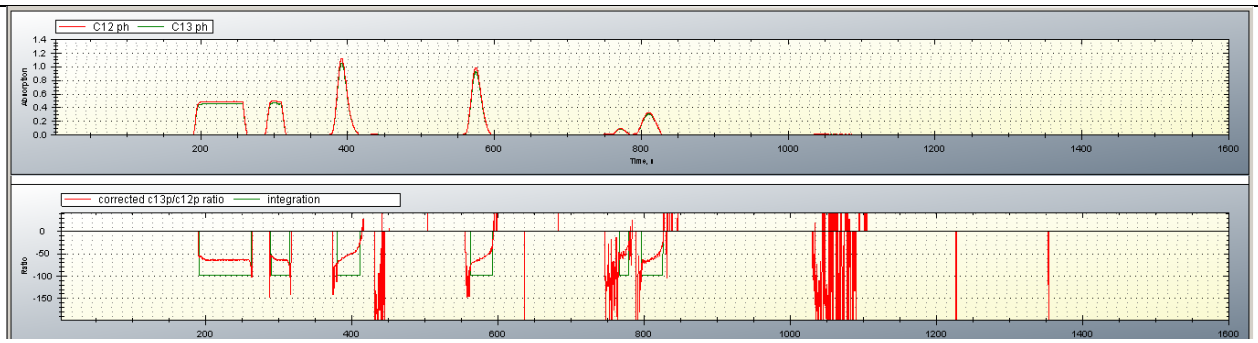


Figure 1a. GC run with two reference pulses ahead of the chemical elute peaks (starting at 400sec) for GC-IR2

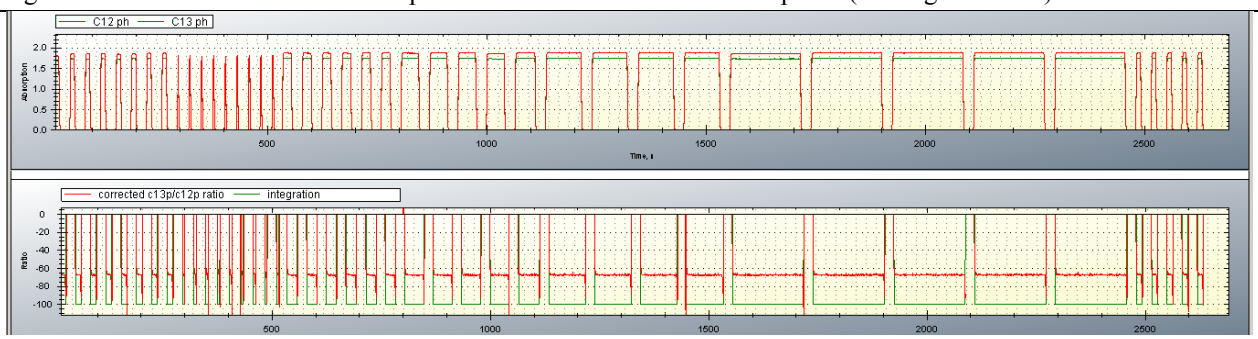


Figure 1b. GC run with reference pulses for IR2 which demonstrates pulse fractionation in Figure 2.

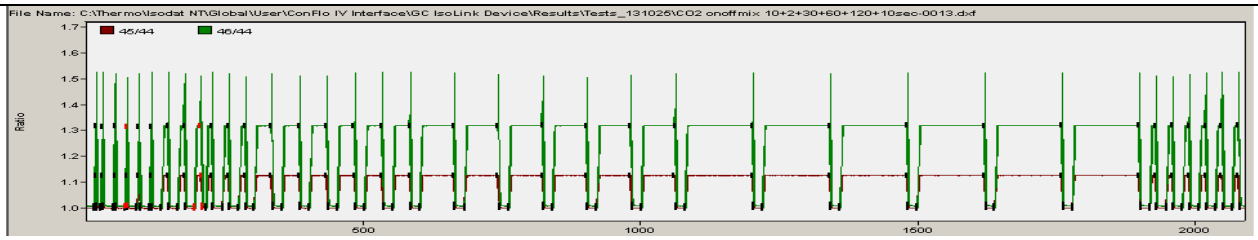


Figure 1c. GC run with reference pulses for Delta-V IRMS which could barely demonstrate pulse fractionation.

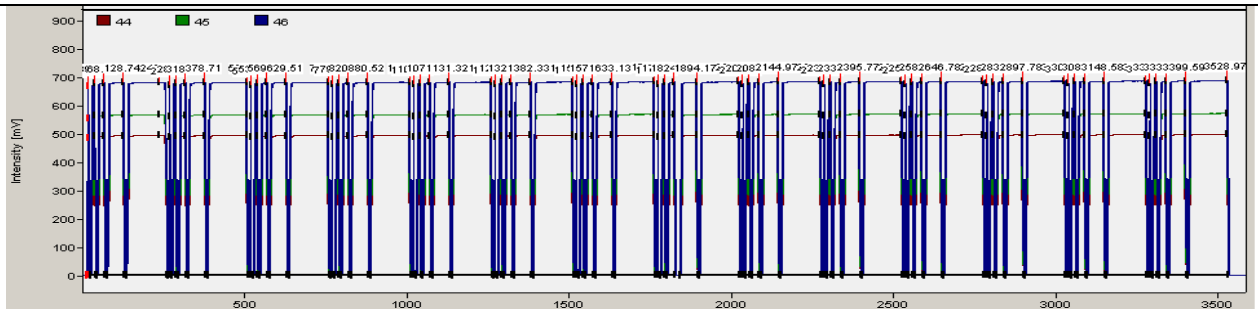


Figure 1d. GC run with reference pulses for Delta-V IRMS which could demonstrate pulse fractionation.

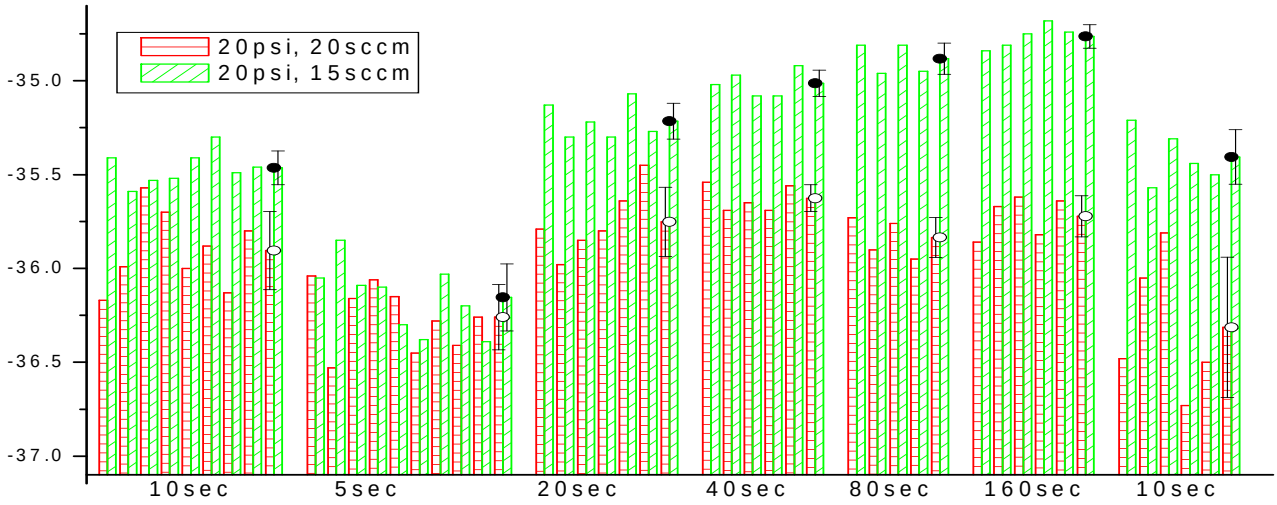


Figure 2a. Low backing pressure for the reference gas pulses, 20psi. Each group of pulses with the same pulse width are separated by a blank data point and the last two are the averaged results of each pulse width group in each GC run, with the standard deviation error bar also included by the data point marker on the averaged point.

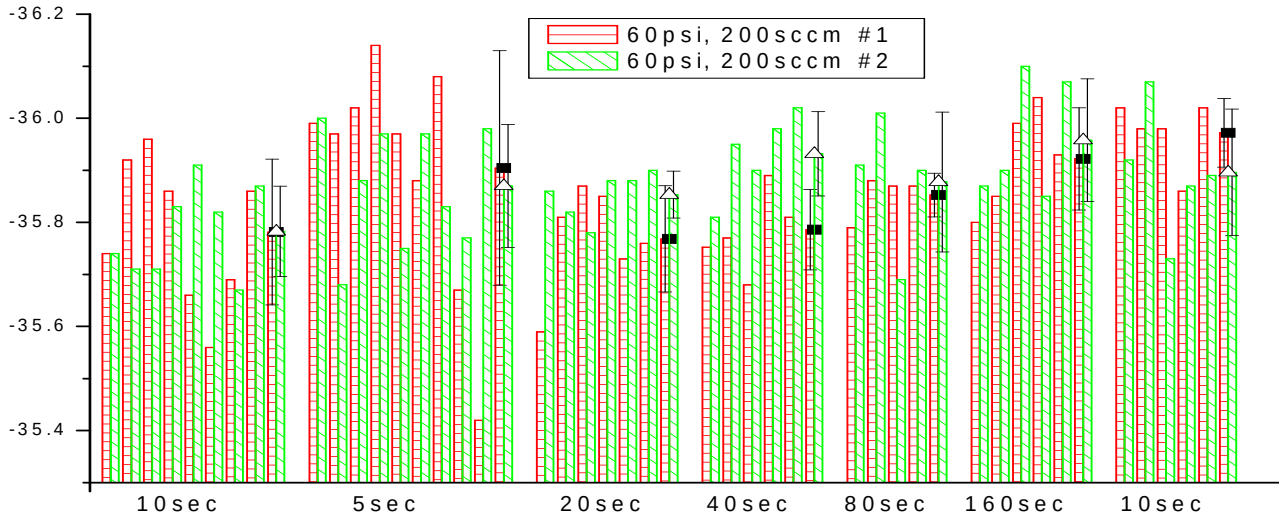


Figure 2b. High back pressure for the reference gas stream, 60psi. The fractionation due to pulse width is much reduced. The standard deviation of the IR2 spectrometer during a 10 minutes period is comparable to that of the IRMS.

The pattern of fractionation also depends on the backing pressure and flow rate of the switching valve which generates the reference pulses. In general, the higher the backing pressure and faster flow will reduce the fractionation. The results are presented in figure 2a and 2b. The minimal observable fractionation is close to the standard deviation of the IR2 spectrometer, i.e. 0.3‰. This shows the accuracy and precision of the IR2 spectrometer are very close, i.e. the drift over an hour is close to its standard deviation in <10 minutes.

Then, we want to verify the existence of such fractionations versus reference pulse widths and generation conditions, i.e. pressure and dilution flow, in the standard GC-IRMS system (Thermo, Delta V). We first generated a series of

reference pulses in a GC run for GC-IRMS system as shown in figure 1c. But we do not observe the same pattern in the measured results (figure 3a) as in our GC-IR2 system (figure 2a, and figure 2b).

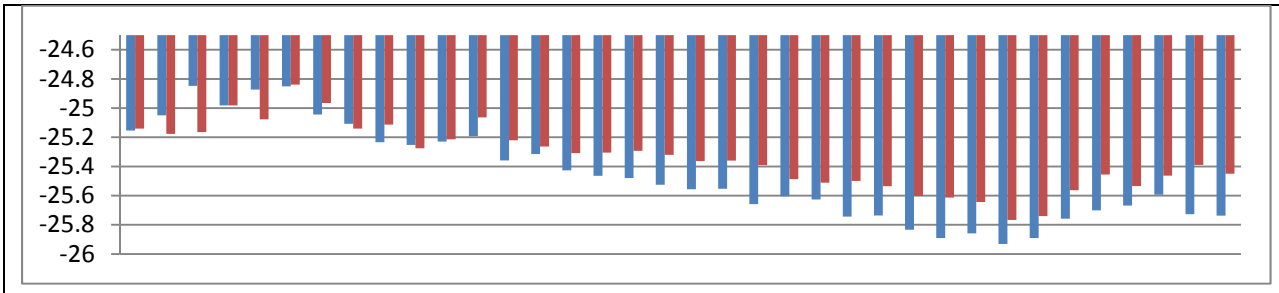


Figure 3a. Fractionation versus pulse width is not obvious with a series of reference pulses from Figure 1c. To GC runs with reference pulses in figure 1c are presented here.

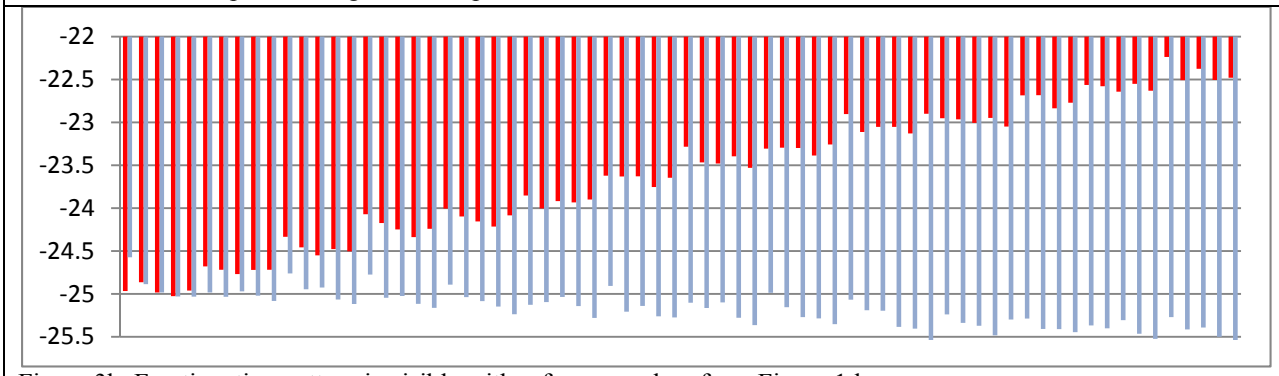


Figure 3b. Fractionation pattern is visible with reference pulses from Figure 1d.

The most obvious difference is that the last pulse group with the same shorter pulse width, i.e. 10sec, as the first group failed to reach the same $^{13/12}$C values as the first group. This is related to the drift of the IRMS system in over 15 minutes, which is well known. In fact, this GC-IRMS mode, or online continuous flow (CF) measurement has a specified accuracy about an order of magnitude worse than constant calibration mode, i.e. dual beam mode IRMS[6]. Schemes to moderate such drift, e.g. bring in a reference on a more regular basis, i.e. every 20 minutes[7], could improve the accuracy. Due to the drift over an hour, the measurement results in figure 3a do not unequivocally validate the fractionation during reference pulse generation as the pulse width changes. The drift is estimated to vary as large as >1‰ in one hour period as we demonstrated below, therefore preventing the easy observation of the fractionations less than 0.5‰. To further verify such fractionations in GC-IRMS system, we applied a different kind of GC run with 5 reference pulses of 5 different pulse widths, i.e. 5sec, 10sec, 20sec, 50sec, 120sec, in a consecutive group, and then repeat this group 12 times in about 1 hour time (figure 1d). The results of two such GC runs taken at 5 hours apart are shown in Figure 3b. We could see that there is an approximate repeating pattern of the ratio values of each group of 5 pulses; but there is a strong drift in baseline in one GC run while not that strong in the other GC run. To better illustrate the repeating pattern of the ratio values of each group of 5 pulses, we then average the results of these 12 groups in Excel sheet by summing up the reference pulses in each group with the same pulse width and divided by 12. The results are shown in figure 4a through 4h for different reference pulse generation conditions. The repeating patterns are now obvious, but come with a baseline shift. Each of the plots in figure 4 has two series, taken at different time usually separated over 6 hours in a day, which have baseline levels separated by as large as 1‰, again a result of the drift of the IRMS system.

. To better illustrate the baseline drift of the GC-IRMS system, we also repeat this 1 hour GC run for over dozen times, i.e. over half a day. We characterized the system drift in a 24 hour period by plotting out the ratio of *m/z* 45 over *m/z* 44, as shown in figure 5b, which is the actual ratio of $^{13/12}$C without calibration of the reference pulses at the

beginning of each GC run. The drift plot in figure 5b shows over 15 ‰ change in 24 hour period, probably related to the ~6°C temperature change of the room where the GC-IRMS is hosted. As a comparison, the GC-IR2 system, which is also hosted in a room with daily temperature variation ~6°C, the drift in actual ratio of $^{13/12}$C is only <1 ‰ as shown in figure 5a. There are several bumps with variation larger than 1 ‰ in figure 5a which lasts over 30 minutes, and they come in synch with the intentional sudden heating and cooling of the room temperature by over 5°C each way. We could see that the stability of the IR2 system during fast temperature change is obviously more robust than IRMS, and we expect the drift could be further reduced to less than 0.5 per mil even when we have 15°C swings each way, i.e. from 5°C to 35°C, in room temperature.

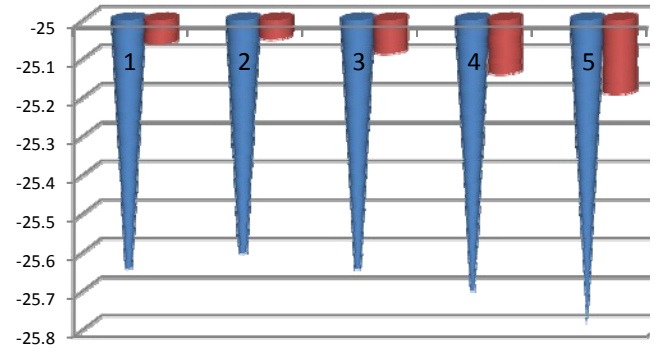


Fig. 4a. Reference pulse generated at 15psi, 5,000mV dilution

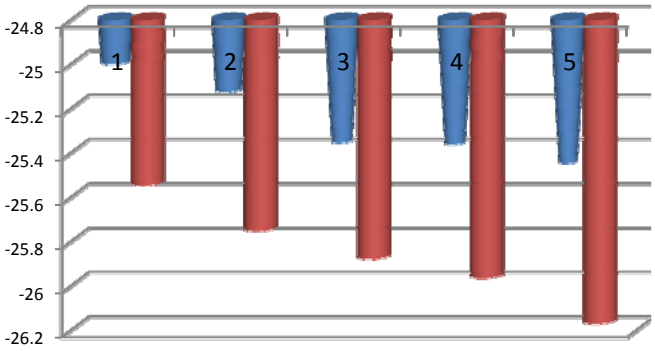


Fig. 4b. Reference pulse generated at 15psi, 500mV dilution

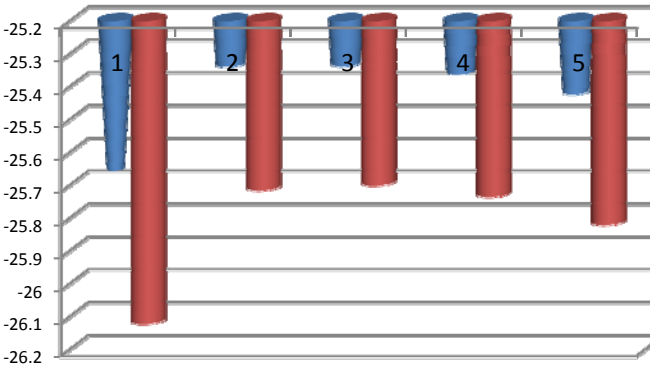


Fig. 4c. Reference pulse generated at 25psi, 5,000mV dilution

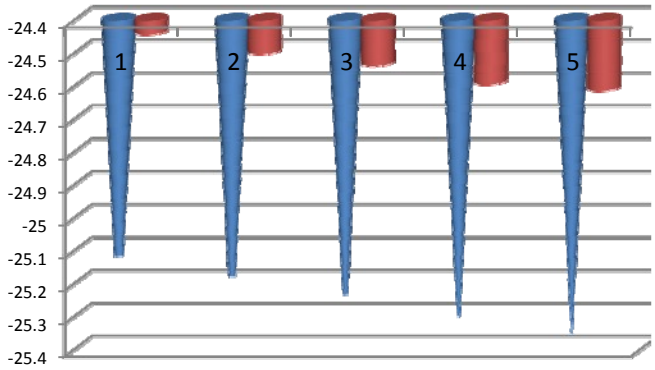


Fig. 4d. Reference pulse generated at 25psi, 500mV dilution

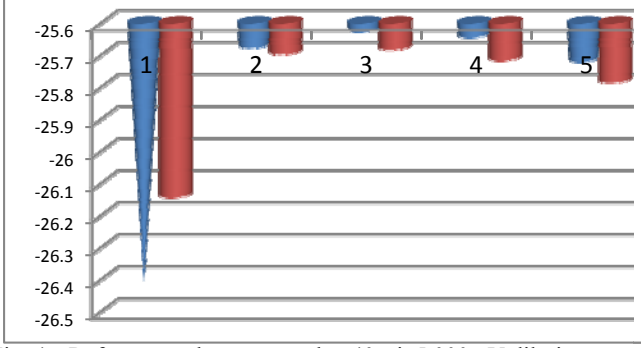


Fig. 4e. Reference pulse generated at 40psi, 5,000mV dilution

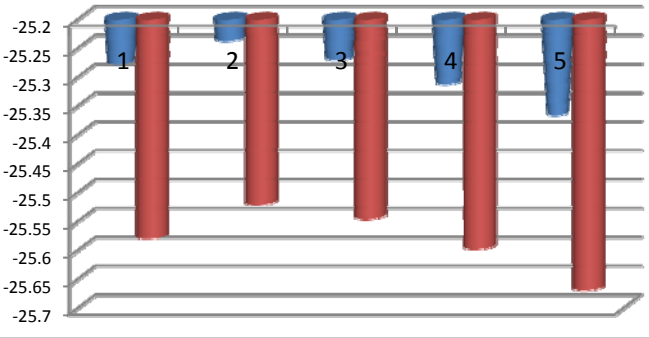


Fig. 4f. Reference pulse generated at 40psi, 500mV dilution

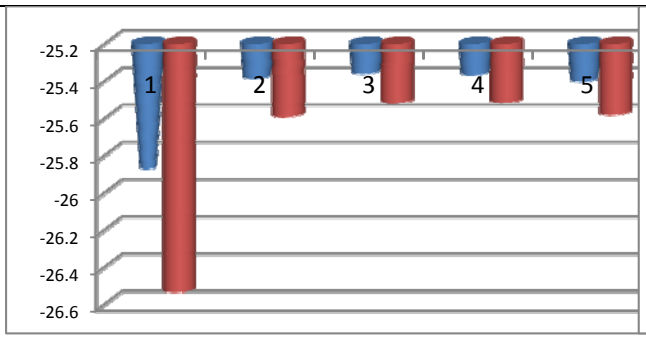


Fig. 4g. Reference pulse generated at 58psi, 5,000mV dilution.

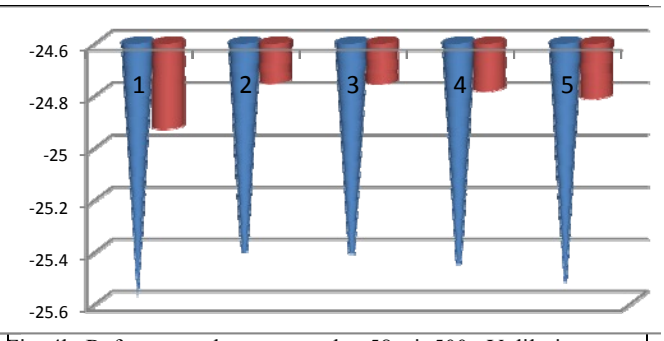
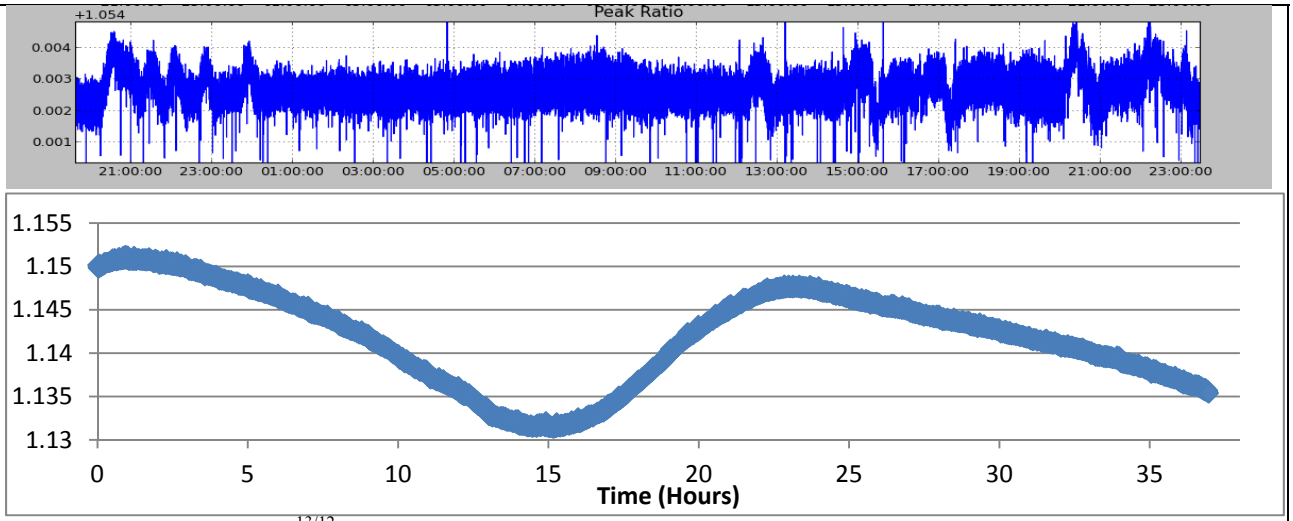


Fig. 4h. Reference pulse generated at 58psi, 500mV dilution



Top, figure 5a. Instrument $^{13/12}$C drift before calibration measured on IR2 spectrometer over ~28 hours; Bottom, figure 5b. Instrument $^{13/12}$C drift before calibration measured on IRMS over ~36 hours.

DISCUSSIONS

Advantages and disadvantages of the IR2 sensor

IR2 spectrometer is based on strong optical absorption in the Mid-Infrared, therefore, it has advantages and disadvantages over IRMS. The advantages include the easy differentiation of isotopomers with the same mass, e.g. $^{13}CO_2$ versus $^{12}C^{17}O^{16}O$. But, it could not detect molecules without strong IR active absorption features, e.g. H_2, or H_2O. The future development of room temperature THz lasers and detectors in the 200cm^{-1} range could enable the detection of H_2O there with IR2, but not yet practical right now.

The stability of the IR2 spectrometer is inherent due to the underlining optical absorption nature of the instrument. This inherent property lends to the easy observation of fractionation in reference pulses as the conditions of pulse generation are varied.

The precision of the IR2 spectrometer is also getting close to that of IRMS. Although the sample amount needed is still larger than MS, it is already below 10μL (Standard Pressure and Temperature), making it compatible with GC operation. The small volume makes calibration easy to carry out in the field. The small sample volume, i.e. <10μL (standard temperature and pressure, STP) makes our IR2 spectrometer unique when compared to other well-known

optical absorption based instruments with larger sample volumes, e.g. cavity enhanced and multipass cell absorption spectroscopy platforms all have sample volume larger than 1ml STP.

CONCLUSION

We varied the reference pulse width, backing pressure and flow rate, and carefully measured the isotopic ratios of the reference gas pulses using both Isotope Ratio Mass Spectrometer (IRMS) and our newly developed Infrared Isotope Ratio (IR2) spectrometer. Results from both instruments demonstrated the existence of the variations in isotopic ratio as the pulse width, backing pressure and flow rate are varied. However, IR2 has better stability over longer period of time, i.e. >1,000 seconds, and therefore better divulge such variations, and give better guidance in generating more consistent and accurate reference pulses. The demonstrated stability translates directly into accuracy of the IR2 instrument, and bodes well for a calibration free or minimal calibration CSIA instrument which fits best for field deployment.

ACKNOWLEDGEMENT

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